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TRANSIENT PHENOMENA FOLLOWING PRECIPITATION AND RE-SOLUTION ANNEALS IN A NiTi ALLOY

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13. ABSTRACT (Maximum 200 words)

Transient phenomena following anneals in a near stoichiometric NiTi alloy are investigated by means of differential scanning calorimetry (DSC). Precipitation anneals (350°C) raise the temperature range of the martensite and R-transformation. Subsequent cycling through the transformation range (-40° to 100°C) produces small changes in the martensite DSC peaks and no observable change in the R-peak. Subsequent re-solution anneals (600°C) produce dramatic effects: M_s rises approximately 20°C above its value preceding the precipitation anneal and the martensite DSC peak is very sharp and symmetric, while the R-transformation peak is not observable. During ensuing cycling, the martensite peak returns to its original form and position after about 300 cycles, and the R-peak appears after 4 cycles and is essentially invariant to cycling. The transient data are consistent with a dislocation model.

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Differential Scanning Calorimetry, Shape Memory Alloys, Martensitic Transformation, Phase Transformation

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INTRODUCTION

Martensite transformations play an important role in determining the properties of many technically important materials, ranging, for example, over ferrous alloys, thermoelastic materials, ferroelectrics, ceramics, and high-T_c A15 alloys. Among the most interesting of these materials are the thermoelastic martensites, which include shape memory effect (SME) and superelastic alloys.

The NiTi alloys (Nitinol), first studied in detail by Buehler et al. (ref 1) and Wang et al. (ref 2) at the Naval Ordnance Laboratory, constitute the most celebrated SME system. Besides the martensite transformation, Nitinol alloys undergo a "premartensite transformation" referred to as the R-transformation. The R-transformation, first described by Wang et al. (ref 2) and Dautovich and Purdy (ref 3), converts the high temperature cubic CsCl structure, B2, to a rhombohedrally distorted CsCl structure, referred to as the R-structure or R-phase. The R-transformation start temperature will be denoted T_R here.

A variety of irreversible phenomena associated with dislocations, precipitates, ordering effects, and residual stresses from previous cold work and/or thermal histories complicate the exploitation of SME alloys. These phenomena are usually studied by measuring electrical resistivity changes (refs 4-6) that occur during phase transformations, and by diffraction (refs 7-9), and metallographic examination (ref 10) of the phases produced by various thermomechanical treatments.

Differential scanning calorimetry (DSC) (refs 11-13) is, although less commonly applied, also used to study effects of thermomechanical processing on phase transformations in SME alloys. DSC complements standard analysis, and is well-suited to quantitative investigation of transient effects.

This report describes a DSC investigation of the properties of a nominally stoichiometric NiTi alloy. Phenomena studied include:

1. The effects produced by a 2-hour anneal at 350°C and subsequent thermal cycling through the range of temperatures from -40° to 100°C.

2. The effects produced by a 2-hour anneal at 600°C and subsequent thermal cycling through the range of temperatures from -40° to 100°C.

3. Transformation behavior of metastable mixtures of martensite and R- and B2-structures formed by interrupting the martensite and martensite-to-B2 phase transformations.

Mechanisms are proposed to explain the observations.

EXPERIMENTAL DETAILS

Data were obtained with a Dupont 1090 Thermal Analysis System, including a DSC module, liquid nitrogen cooling accessory, and mechanical cooling accessory (MCA). Argon atmosphere was employed for all runs. No sample pans or references were employed. The MCA provided sufficient cooling capacity to perform linear cooling at a rate of -5°C/min to temperatures as low as -40°C, and was employed in all the thermal cycling and interrupted transformation studies reported here. The thermal cycling results were obtained at rates of ±5°C/min; the interrupted transformation studies were performed at ±1°C/min. The heat flow calibration is based upon specific heat determinations on an Al_2O_3 standard; the heat flow values shown in the figures must be multiplied by 0.82 to obtain "calibrated values."

The sample was cut with a diamond saw from a nominally stoichiometric NiTi ingot supplied by Titanium Metals Corporation, which had been employed as a source of material for an earlier investigation by Milligan (ref 14). The cut sample was annealed for 2 hours at 600°C, and was then cycled between 77° and 373°K until no changes in peak positions were detectable. Sample mass was 53 mg. A starting material DSC curve obtained employing the MCA and heating and cooling at 5°C/min is shown in Figure 1.

EXPERIMENTAL RESULTS

Anneal at 350°C (Precipitation Anneal)

Figure 2 shows the 1st, 6th, 22nd, and 28th thermal cycle R and martensite transformation DSC peaks following a 2-hour anneal at 350°C. The following effects, most of which may be seen by examination of Figures 1 and 2, are produced by a 2-hour anneal at 350°C:

Immediate Effects:

1. The martensite transformation moves approximately 10°C higher in temperature.

2. A shoulder is seen on the low temperature side of the post-anneal peak, near the pre-anneal martensite DSC peak temperature.

3. The R-transformation peak and the (heating) martensite-to-B2 transformation peak (not shown in Figure 2) are essentially unchanged in shape and move to temperatures approximately 12°C higher than before the anneal.

Effects of Thermal Cycling Following the 350°C Anneal:

1. The martensite peak moves to lower temperatures.

2. The martensite peak sharpens a bit, i.e., M_S-M_F decreases.

3. The low temperature shoulder on the martensite DSC peak persists.

4. The R-transformation peak and the martensite-to-B2 transformation peak (not shown) are essentially unchanged by thermal cycling.

5. No further changes are seen after about 25 thermal cycles.

Anneal at 600°C (Re-solution Anneal)

The dramatic results produced by annealing for 2 hours at 600°C following the 350°C precipitation anneal and thermal cycling are illustrated in Figure 3.

Immediate Effects:

1. Direct transformation from B2-structure to martensite occurs. (That is, $M_S > T_R$ and no intermediate B2-to-R phase transformation is seen during the first thermal cycle following the re-solution anneal.)

2. M_S is raised about 20°C above its value preceding the 350°C anneal.

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3. The martensite transformation peak is very sharp relative to its original form, i.e., M_S-M_P decreases substantially.

4. The martensite-to-B2 transformation DSC peak is essentially unchanged from its shape and position before the 600°C anneal, i.e., it remains approximately 12°C higher than its position previous to the 350°C anneal.

Effects of Thermal Cycling Following the Re-solution Anneal:

1. The martensite transformation peak moves monotonically to lower temperatures, broadens (M_S-M_P increases), and becomes more asymmetric as thermal cycling proceeds.

2. The R-transformation DSC peak emerges as a high temperature shoulder on the martensite transformation peak after 5 thermal cycles.

3. The R-transformation DSC peak is split entirely off the martensite peak after about 15 cycles.

4. Although there is an apparent small increase in the critical temperatures for the R-peak with thermal cycling, the R-transformation peak is essentially invariant under thermal cycling.

5. The martensite-to-B2 transformation moves monotonically to lower temperatures.

6. The transformation peaks are essentially unchanged by further cycling after about 250 cycles.

7. After 250 thermal cycles, all the transformation peaks are within about 3°C of their positions before the 350°C precipitation anneal.

Interrupted Transformation Results

Interrupted Martensite Transformation

The results of a typical series of DSC measurements illustrating the transformations upon heating of mixtures of martensite and R-phase ranging from 0 to 100 percent martensite formed by interrupting the martensite transformation are shown in Figure 4. The interruptions are in order of increasing martensite. The following effects are found:

1. The most conspicuous feature of these experiments is the appearance of the reverse R-transformation (i.e., R-to-B2 transformation) peak.

2. The area (i.e., enthalpy) of the reverse R-transformation peak correlates with the amount of retained R-phase.

3. The area of the martensite-to-B2 peak correlates with the amount of martensite formed. (The area balances would probably be exact if the DSC peaks could be interpreted during the interruption.)

4. The shape of the martensite-to-B2 transformation peak varies according to the amount of martensite formed.

5. The position of the martensite-to-B2 peak shifts to higher temperature as the amount of retained R-phase increases, which strongly suggests that the first formed martensite is the last to transform to B2-phase.

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6.   The differences in the heating baselines are a real effect and reflect the difference in specific heat of martensite and R-phase.

7.   The reverse R-transformation peak position is insensitive to the amount of retained R-phase.

8.   There is no trace of an anomaly during cooling through the temperature of the previous interruption in the martensite transformation.

9.   There is no indication of a martensite-to-R transformation.

Interrupted Martensite-to-B2 Transformation

The results of a typical series of DSC measurements illustrating the transformations on cooling of mixtures of martensite and B2-phase ranging from 100 to 0 percent martensite formed by interrupting the martensite-to-B2 phase transformation are shown in Figure 5. The interruptions are in order of decreasing martensite. The following effects are found:

1.   The area of the R and martensite transformation DSC peaks correlates with the amount of B2-phase formed.

2.   The B2-to-R phase DSC peaks obtained in the martensite-B2 mixtures are essentially reduced-scale versions of those obtained in the 100 percent B2 case so that the shape and position of the R-transformation peak appears insensitive to the presence of retained martensite.

3.   The martensite transformation peak is distorted by the presence of retained martensite:

      a.   The "nearly 100 percent retained martensite" cases seem to be special. For the "nearly 100 percent retained martensite" cases, the martensite transformation is concentrated on the low temperature side of the martensite transformation range, and the R-transformation is too small to be observed. (The limit on the amount of B2-phase corresponding to "nearly 100 percent retained martensite" is shown in Figure 5.)

      b.   For all other cases, the initial reaction rate appears to be identical to that in the zero percent retained martensite case. That is, the initial reaction rate is apparently independent of the presence of retained martensite.

      c.   The temperature at which the reaction rate is maximum is essentially invariant to the presence of retained martensite.

      d. M_s and M_f are essentially insensitive to the presence of retained martensite.

4.   Anomalies are apparent in the martensite-to-B2 structure transformation DSC peaks as the temperature passes through the previous interruption temperature. Features of the anomalies include:

      a.   Sharply reduced reaction rate occurs at the previous interruption temperature.

      b.   In the cases where sufficient temperature increases occur, the reaction rate shoots up to values significantly higher than those observed in the uninterrupted case. Although not shown in Figure 5, the increased reaction rate is such that the amount transformed catches up to the noninterrupted case, and the end of the martensite-to-B2 peak is essentially retraced.

DISCUSSION

Discussion of Annealing and Thermal Cycling Effects

The power of the DSC approach is illustrated by the abundance of experimental results described in the previous section. The DSC results are complementary to the usual resistance studies. In the resistance technique, one measures changes that are governed by differences in the resistivity of the phases and possibly by their configurations; the change in resistance associated with the R-transformation is of the same order as that associated with the martensite transformation. In the DSC approach, the signals are associated with enthalpy differences and reaction rates; the R-transformation DSC peak is substantially smaller than the martensite transformation DSC peak.

Rather than analyzing each experiment in isolation and subsequently attempting to synthesize a coherent basis for all the data, the results are addressed, a posteriori, in terms of a set of proposed mechanisms. Although we have some misgivings with regard to proposed mechanism No. 4, since it is not clear that nickel-rich compounds should precipitate out of an essentially stoichiometric NiTi matrix, all the data are consistent with the given framework.

The following mechanisms are proposed to operate in near stoichiometric NiTi, which has not been subjected to any mechanical processing:

1. Dislocation stress fields strongly influence the martensite and martensite-to-B2 transformations.

This is a natural extension of the well-known sensitivity of martensite transformations to stresses. The existence and importance of "stress-induced martensite" is well-known. The importance of dislocation stress fields in the interpretation of thermomechanical treatment of NiTi alloys has been stressed in the work of Miyazaki et al. (ref 6).

2. Thermal cycling in the transformation range (-40° to 100°C) produces dislocations.

Miyazaki et al. (ref 6) employed transmission electron microscopy to demonstrate that thermal cycling yields increased dislocation density in NiTi alloys. They also argued in favor of a dislocation mechanism in thermal cycling by a process of eliminating other possibilities (viz., aging or ordering phenomena). Thus, Miyazaki et al. ascribed the following effects of thermal cycling in NiTi alloys (which had not been subject to any mechanical processing) to increasing dislocation density:

   a. The martensite transformation peak and, in particular, M_s and M_F, move monotonically to lower temperatures with increasing dislocation density.

   b. The martensite transformation peak broadens (M_s-M_F increases) with increasing dislocation density. The latter effect is presumably a result of the increasing level of the maximum stress intensity (which gives rise to a larger variation of the stress within the specimen) with increasing dislocation density.

The effects of thermal cycling in our experiments are described above. All these effects are consistent with the dislocation production hypothesis:

   a. All the effects of increased dislocation density (other than the transmission electron microscopy) enumerated in Reference 6 are observed.

   b. *Similar phenomena associated with the martensite-to-B2 transformation peak are also observed during thermal cycling.*

c.   Similar phenomena associated with the B2-to-martensite transformation peak, which may be observed immediately after re-solution treatment, are also observed during thermal cycling. Note that the observation of changes through about 250 thermal cycles in the present work is consistent with the observed changes through about 100 cycles in Reference 6.

N.b., although the present results strictly pertain to a dislocation distribution engendered by thermal cycling through the range of temperatures from -40° to 100°C (which we refer to as a thermal cycling-produced dislocation distribution), the results of Reference 6 suggest that they also hold for plastic deformation-produced dislocation distributions. If this is correct, it would seem that inhibition of the martensite transformation, etc., might better be described as produced by changes of dislocation mobility rather than of dislocation stress fields. The discussion is, nevertheless, presented in the context of dislocation stress field action.

3.   Dislocation stress fields have a weak effect on the B2-to-R and R-to-B2 transformations.

This assertion follows from a combination of Item Nos. 1 and 2 directly above, and the observations cited under the Experimental Results section also above. This conclusion is also supported by the results in Reference 6 generally and particularly those shown in Figure 4 of Reference 6.

This assertion runs contrary to the conclusion of Goldstein et al. (ref 13) that stress fields are required to stabilize the R-phase. (See Item No. 7 below.)

4.   Precipitation of nickel-rich compounds and possibly a thermal rearrangement of dislocations takes place during annealing at 350°C.

The argument for this item goes as follows:

a.   The R-transformation peak temperature increases by more than 10°C following the 350°C anneal.

b.   The critical temperatures of the transformation peaks in NiTi SME alloys *increase* with *decreasing* nickel concentration.

c.   Therefore, since Items Nos. 1 through 3 imply that dislocation structure cannot be responsible for the increase of T_R, and since ordering effects are not observed even after the 600°C anneal, the increase of T_R is the result of a decrease in the matrix nickel concentration.

d.   The distorted form of the martensite transformation and its persistent low temperature shoulder suggest that a modified dislocation structure is also produced by the 350°C anneal. Further arguments in favor of dislocation rearrangement at 400°C may be found in Reference 6.

The persistent shoulder on the martensite transformation peak following the 350°C anneal, which appears in the range of temperatures where the martensite transformation peak was observed before the 350°C anneal, suggests that stabilized precipitate-free regions remain after the 350°C anneal.

A possible problem with this interpretation arises since it is not evident that precipitation of nickel-rich compounds should reduce the free energy of stoichiometric NiTi. Miyazaki et al. (ref 6) found precipitates

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following 400°C anneals in their nickel-rich samples, but *not* in a $Ni_{49.8}Ti_{50.2}$ sample. Although the disposition of the transformation peaks in our alloy are consistent with stoichiometric NiTi, it is possible that our material is slightly nickel-rich.

5. Recrystallization and re-solution of nickel-rich compounds occurs during the 600°C anneal.

This mechanism was proposed by Goldstein et al. (ref 13) for 600°C annealing in the nickel-rich alloy they studied. Also, the observations here are of the same form as those of Reference 6 following their 1000°C "solution anneal." Furthermore, the present data exhibit the following effects consistent with Item No. 5:

a. The characteristic temperatures of the martensite transformation achieve their highest values, which are consistent with the lowest dislocation densities (see the discussion of Item No. 2 above.)

b. The initial stages of thermal cycling produce rapid changes in the martensite and martensite-to-B2 peaks, which are consistent with dislocation production in a precipitate-free region of initially low dislocation density.

6. The presence of precipitates and/or a pre-existing dislocation distribution inhibits dislocation production during thermal cycling.

This hypothesis is, of course, nothing new. However, it allows one to explain the facts that after the 350°C anneal, which leaves a relatively high dislocation density plus precipitates, transient phenomena span about 25 thermal cycles, while following the 600°C anneal, which leaves a relatively low dislocation density and no precipitates, transient phenomena span about 250 thermal cycles.

7. The R-phase is *not* (significantly) stabilized by dislocation stress fields.

Item No. 7 follows from the fact that T_R is essentially independent of the stress fields associated with thermal cycling, which implies that the stability of the R-phase is not affected by dislocation stress fields.

Goldstein et al. (ref 13) drew the contrary conclusion based on the following reasoning: B2-phase transforms directly to martensite in NiTi having low enough dislocation density. Thus, dislocation stress fields are required to stabilize the R-phase. Although this conclusion is correct in the sense that the R-phase does become unstable with respect to martensite for sufficiently low dislocation density, it is misleading.

In the light of the thermal cycling results presented here, the straightforward interpretation of the direct transformation of B2-to-martensite is as follows: Stress fields associated with dislocations inhibit the martensite transformation. Thus, the R-phase forms when M_S is low enough relative to T_R.

Discussion of the Interrupted Transformations

The interrupted transformation studies yield a daunting array of phenomena. The analyst is faced with the problem of providing a consistent set of mechanisms that explain the effects of annealing treatments, thermal cycling, and the diverse phenomena associated with metastable mixtures of phases, such as the ones produced by interrupting the martensite and martensite-to-B2 transformations.

The interrupted transformation results are not inconsistent with the collection of mechanisms described above. However, the enumerated mechanisms are not sufficient to explain the observations. We conclude with a discussion of the interrupted transformation results and some ideas that we believe may be germane.

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The reader should keep in mind the alternative interpretation, in terms of changes of dislocation mobilities, alluded to in the last paragraph of Item No. 2 in the previous section.

The R- and Reverse R-Transformations

The shapes of the R-transformation and of the reverse R-transformation (which is observed in the interrupted martensite transformation studies) DSC peaks are insensitive to the presence of retained martensite and retained R-phase, respectively. These results are consistent with the behavior of the R-transformation peak during dislocation production, etc. (See Item No. 3 above.)

The Interrupted Martensite Transformation

Straightforward Interpretation

The interrupted martensite transformation studies are also subject to straightforward interpretation in terms of the enumerated mechanisms, as follows: Martensite forms first in the regions of lowest stress (furthest from dislocations). Martensite transforms to B2-structure first (last) in regions of highest (lowest) stress. Therefore the martensite, which forms first, transforms to B2-structure last as observed.

Retained Phase Interference Model

However, another interpretation, which considers the effects of metastable retained phases, is also consistent with the proposed mechanisms: The martensite-to-B2 transformation occurs in the presence of B2-phase, which was newly formed from the retained R-phase. The presence of B2-phase (and possibly the effects of the reverse R-transformation) produces a modified stress distribution (or dislocation distribution) in the transforming martensite. The greater the percentage of volume occupied by the pre-existing B2-phase, the larger the change in stress distribution, and hence the greater the inhibition of the martensite-to B2 transformation. The change in stress distribution would have to be in the direction of stress relaxation in the transforming martensite, which seems plausible since martensite is associated with larger specific volume.

The Interrupted Martensite-to-B2 Transformation

Straightforward Interpretation

The interrupted martensite-to-B2 transformation studies are most puzzling. The "straightforward interpretation" of the interrupted martensite transformation studies described above does not work in the general case. The B2-phase formed first (after transforming to R-phase) does not transform to martensite last, except in cases in which there is essentially 100 percent retained martensite. The maximum percentage of transforming the R-phase consistent with a "straightforward interpretation" is approximately that for the exceptional curve in Figure 5.

Retained Phase Interference Model

The retained phase interference model interpretation goes as follows: The R-to-martensite transformation occurs in the presence of retained martensite. The presence of retained martensite produces a modified stress distribution (or dislocation distribution) in the transforming R-phase. Thus, the form of martensite transformation in the presence of retained martensite is modified.

This interpretation is not quite satisfactory either, since the essential invariance of M_s, M_p, the temperature for the maximum reaction rate, and the initial total reaction rate are not explained.

Temperature Memory Effect

The anomalies observed in the martensite-to-B2 transformation at the temperature of the previous interruption are spectacular. Less spectacular anomalies can be produced in the martensite transformation, by interrupting and *isothermally holding* at some temperature. Similar effects can be observed in a wider class of materials than thermoelastic martensites.

It seems clear that these phenomena are associated with pre-existing phase boundaries (and their associated dislocation distributions), which were mobile at the interruption temperature at the moment that the interruption occurred. The boundaries (and their associated dislocation distributions) are then stabilized by the ensuing R- and martensite transformations, which occur in the presence of the retained martensite. Thus, the inhibition of the transformation at the interruption temperature and the subsequent increased reaction rate at sufficient superheating are natural consequences of the moving phase boundaries approach toward and through the region at which the old boundaries were "stabilized."

Efficacy of DSC in the Study of Phase Transformations in Thermoelastic Martensitic (SME) Alloys

Resistance methods are routinely utilized in phase transformation studies of shape memory alloys. The resistance of an alloy is governed by the resistivity and disposition of the transforming phases. Sample preparation and processing are relatively simple and the determination of resistance is straightforward. The resistivity of the transforming phases (which is not directly measurable) is controlled by the structure and degree of order of the phases. Resistance changes can be highly sensitive to subtle structural changes. The sensitivity of the resistance to diverse influences is at once a strength and a weakness of the technique: Quantitative analysis is difficult, but subtle effects are revealed.

DSC results complement those obtained in resistance studies. DSC signals are associated with enthalpy differences and reaction rates. Sample preparation is relatively simple, but mechanical processing of DSC samples is not convenient. The strength of the DSC method (assuming that the phases involved have been determined) is that it yields a direct quantitative measure of the progress of a transformation. The power of the DSC approach is illustrated by the abundance of experimental results concerning phase transformations in NiTi shape memory alloys described in this report.

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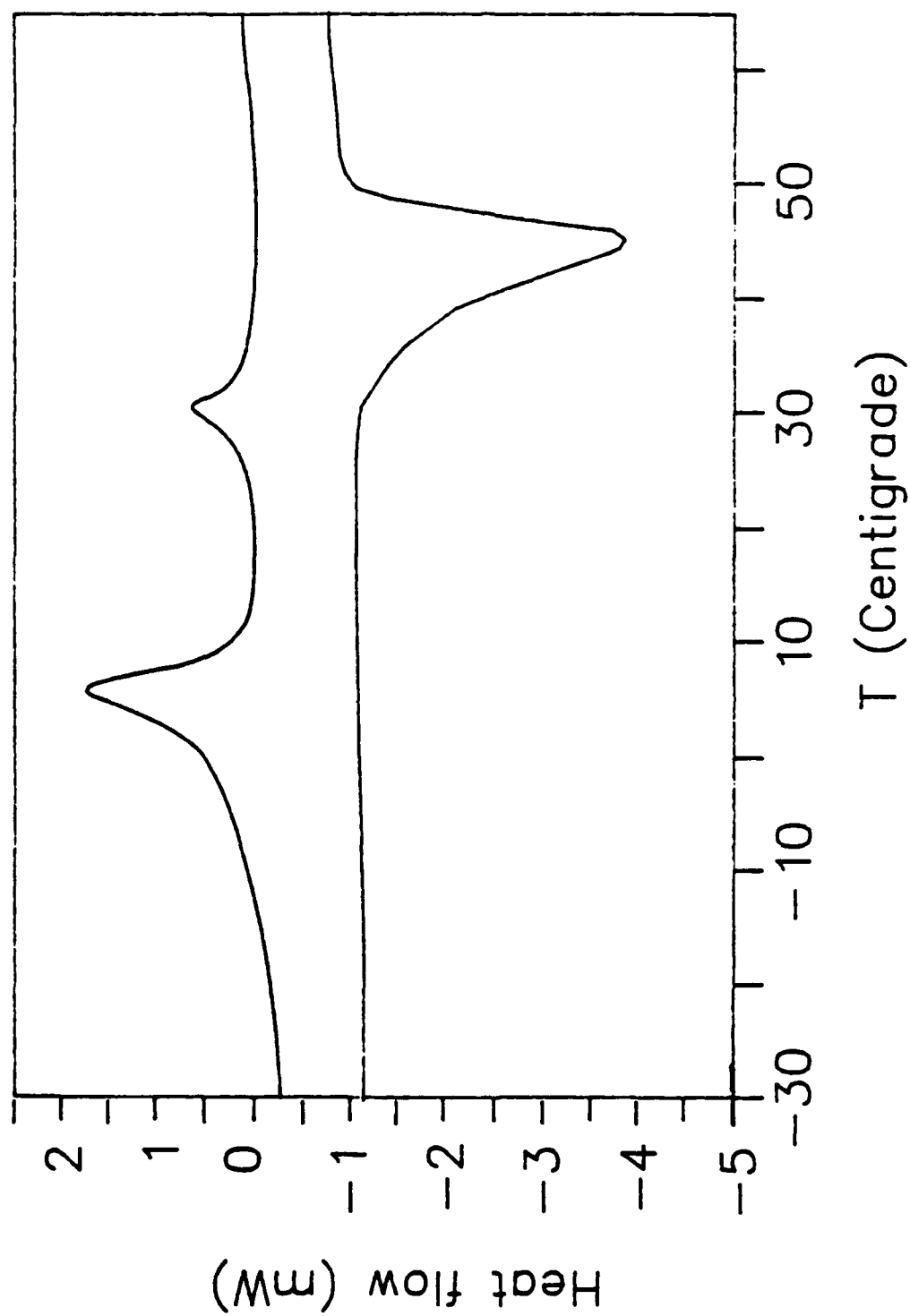
Figure 1. DSC trace for starting material.
Heating and cooling rates are 1°C/min.
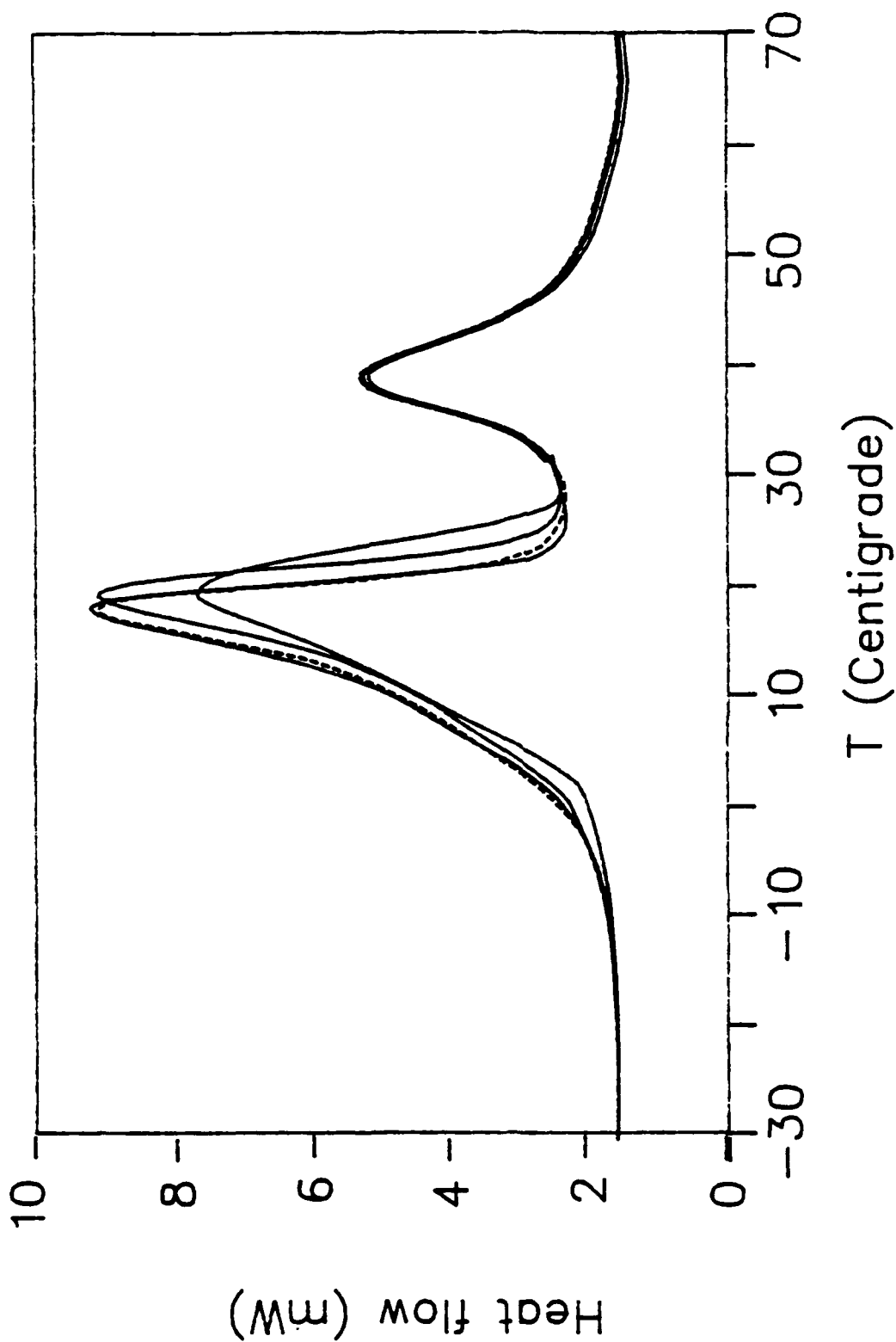Positive heat flow is exothermic on all figures.

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Figure 2. DSC curves subsequent to a 2-hour anneal at 350°C; consequences of the precipitation anneal. The traces shown are for the 1st, 6th, 22nd, and 28th transformation cycles. The sample was cycled between -40° and 100°C at 5°C/min. The difference between the 22nd and 28th transformation cycle traces is barely perceptible. Further cycling yields negligible changes in the DSC trace. (The scale has been chosen to match that in Figure 3.)
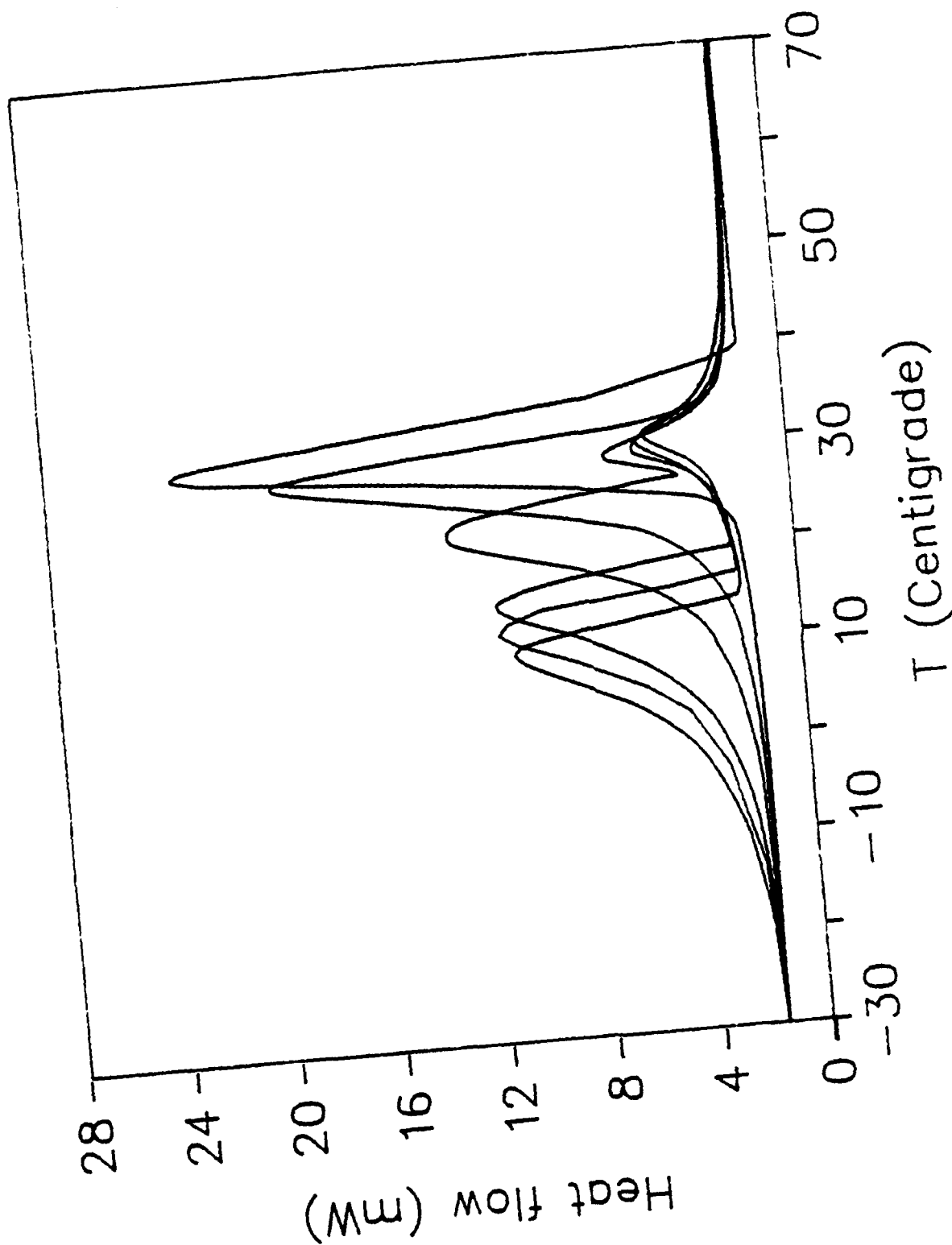
Figure 3. DSC curves subsequent to a 2-hour anneal at 600°C; consequences of the re-solution anneal. The traces shown are for the 1st, 5th, 9th, 28th, 50th, and 94th transformation cycles. Further cycling yields negligible changes in the DSC trace. The sample was cycled between -40° and 100°C at 5°C/min. The R-transformation emerges as a shoulder on the martensite DSC peak on the 6th cycle and moves continuously to higher temperatures with continued cycling.
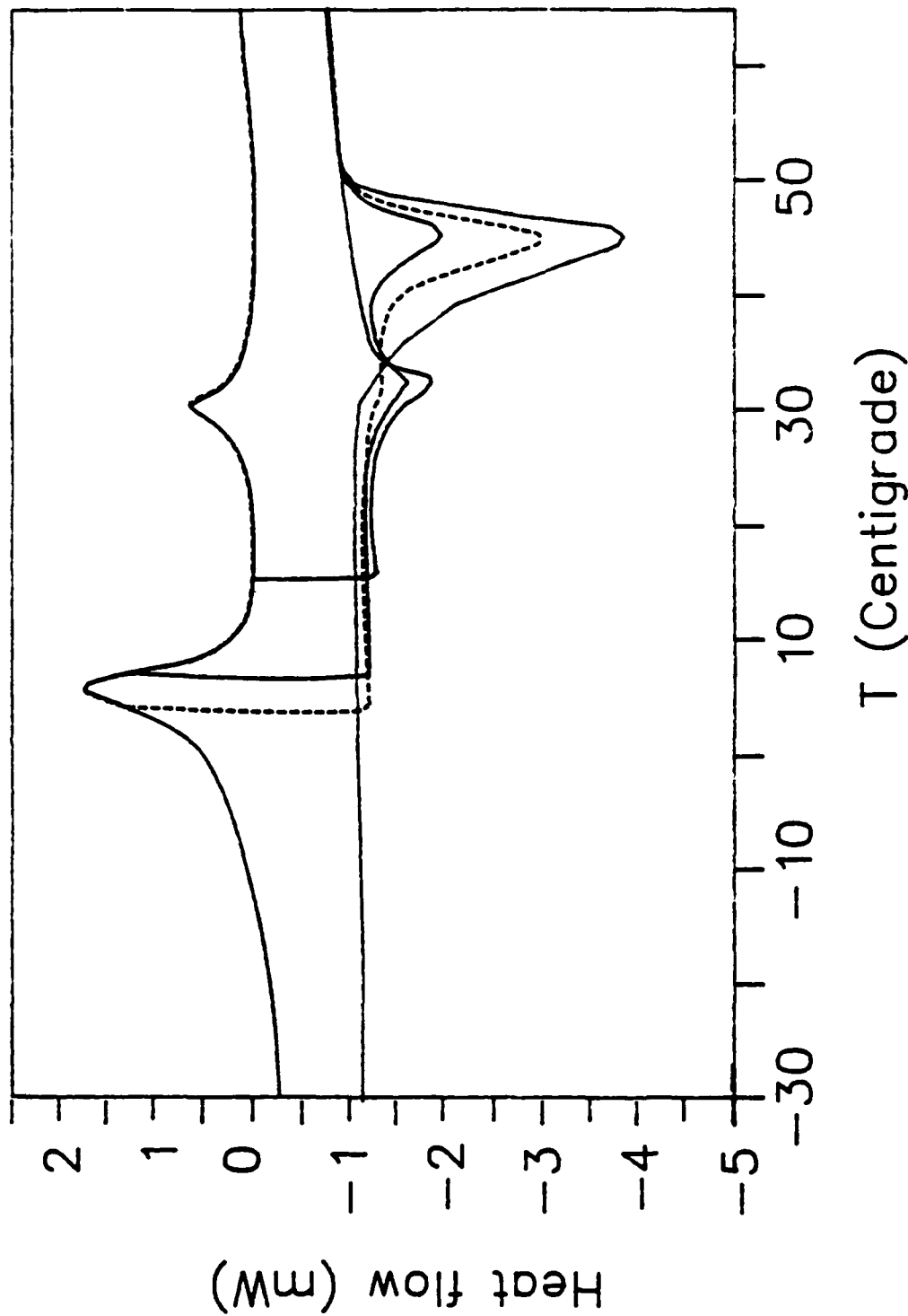
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Figure 4. Interrupted transformation studies. Mixtures of martensite and R-phase prepared by interrupting the martensite transformation are reheated until 100 percent B2-phase is obtained. Heating and cooling rates are 1°C/min. The appearance and area (transformation enthalpy) of the reverse R-transformation peak (R --> B2) correlate with the amount of retained R-phase (proportional to the missing area in the martensite transformation peak). Similarly, the martensite-to-B2 peak area correlates with the area of the interrupted martensite peak. N.b., the small differences in the levels of the heat flow during heating near 20°C are real and reflect the difference in heat capacity of martensite and R-phase.
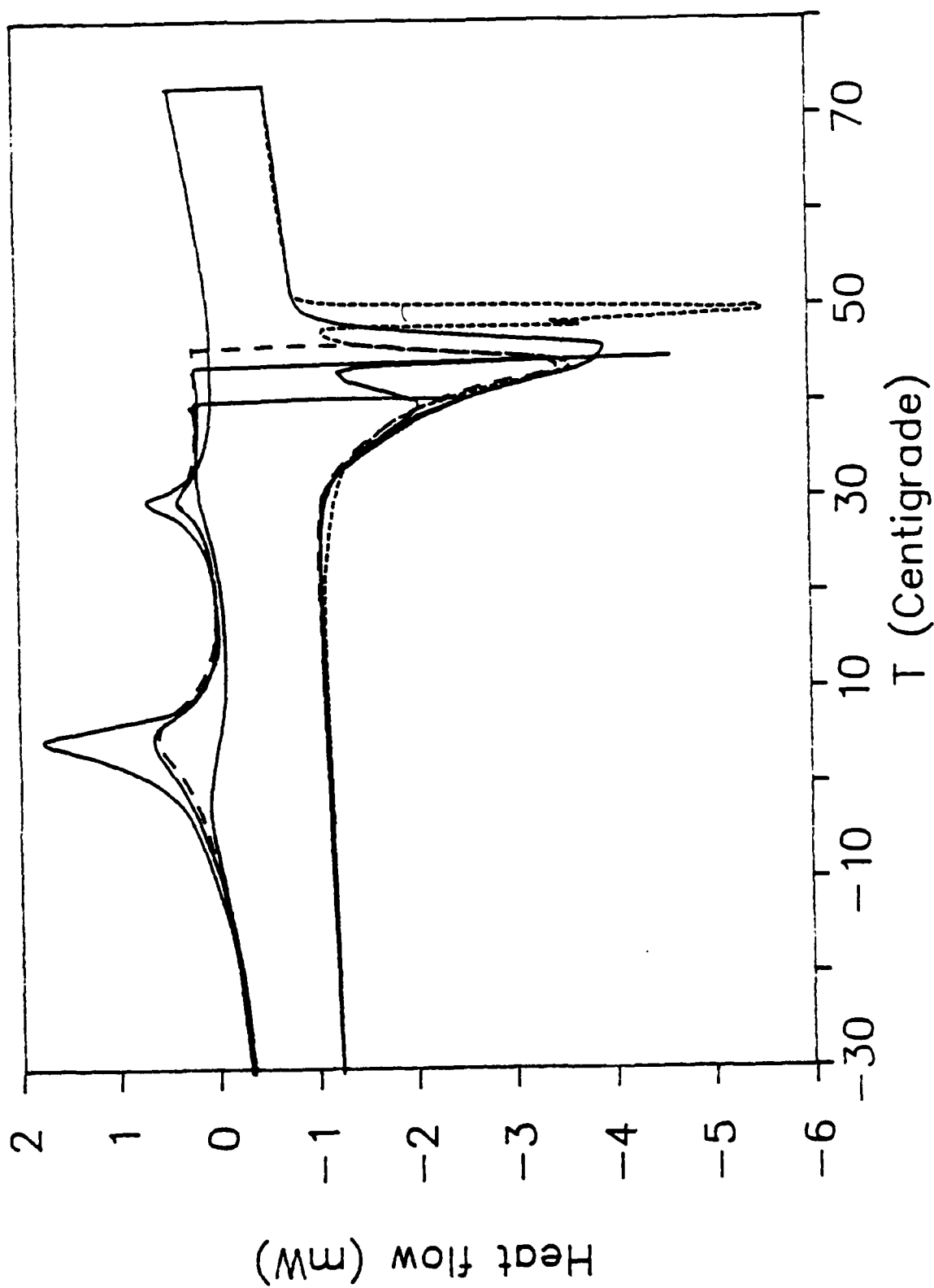
Figure 5. Interrupted transformation studies. Mixtures of martensite and B2-phase prepared by interrupting the martensite-to-B2 transformation are cooled until 100 percent martensite is obtained. Heating and cooling rates are 1°C/min. The area (transformation enthalpy) of martensite and R-transformation peaks (R --> martensite and B2 --> R) correlate with the amount of B2-phase formed.

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